INFRARED ABSORPTION OF CH_3O/CD_3O RADICALS PRODUCED UPON PHOTOLYSIS OF CH_3ONO/CD_3ONO IN A p-H_2 MATRIX

YU-FANG LEE, WEI-TE CHOU, *Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan*; BRITTA JOHNSON, EDWIN SIBERT, *Department of Chemistry, The Univeristy of Wisconsin, Madison, WI, USA*; YUAN-PERN LEE, *Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan*.

The methoxy radical, CH_3O, has attracted much attention because of its important molecular structure and also as a reaction intermediate in combustion and atmospheric chemistry. Previous investigations include laser-induced fluorescence, laser magnetic resonance, and stimulated emission pumping. High-resolution infrared spectrum of jet-cooled CH_3O, produced by laser photolysis of CH_3ONO, in the C-H stretching region 2850-2940 cm^{-1} has been reported.[a] However, direct infrared absorption spectrum of CH_3O other than the C–H stretching region remains unreported. Irradiation of a p-H_2 matrix containing CH_3ONO at 3.2 K with UV light produced main features at 1365.4, 1427.5 (2_1^-, 2_1^+), 1041.8 (3_1^-), 1346.8, 1427.5, 1520.9, 1520.9 (5_1^-, 5_1^+, 5_1^-, 5_1^+), and 689.3/694.9, 945.9/951.7, 1233.5, 1235.9 cm^{-1} (6_1^-, 6_1^+, 6_1^-, 6_1^+); labels 2-6 in parentheses indicate transitions to vibrational states attributable to the umbrella, C–O stretching, CH_2 scissoring, and HCO deformation modes of CH_3O, respectively. These features appeared upon photolysis and diminished after five minutes; formation of CH_2OH was observed as CH_3O decayed. The assignments were based on comparison of observed vibrational wavenumbers with those predicted with the quadratic potential energy force field and quadratic dipole moment expansion calculated with the CCSD(T)/cc-pVTZ method.[b] Jahn-Teller and anharmonic vibrational contributions were included in the full Hamiltonian to estimate the correlation diagram connecting the harmonic eigenvalues to those of the fully coupled problem. Similarly, lines of CD_3O were observed upon UV photolysis of CD_3ONO, but became diminished within five minutes. These observations demonstrates the advantage of diminished cage effect of solid p-H_2; CH_3O and CD_3O are produced via $insitu$ UV photodissociation of CH_3ONO isolated in p-H_2, but not in Ar or Ne.

[a] J.-X. Han, Y. G. Utkin, H.-B. Chen, L. A. Burns and R. F. Curl, *J. Chem. Phys.* **117**, 6538 (2009).

[b] J. Nagesh and E. L. Sibert III, *J. Phys. Chem. A* **116**, 3846 (2012).